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Polaritons at Surfaces

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We calculate the reflectivity of light incident upon the exposed face of a semi-infinite crystal, using the point-dipole model. This requires an accurate solution for the polariton modes near the crystal surface. The variation of the Lorentz local field, caused by the surface, is included in the calculations. The boundary conditions for the polariton modes are derived rigorously. This represents the first rigorous microscopic solution of polariton modes near ideal surfaces.

I. INTRODUCTION

We wish to calculate the transmission and reflection of light incident upon the exposed face of a semi-infinite crystal. The crystal is assumed to be mathematically perfect, with atoms situated in their undisturbed positions in one half-plane, and no atoms in the other half-plane. The atoms of the crystal are assumed to be neutral, polarizable, and infinitesimal in size—i.e., the point-dipole model. Each atom sees a local electric field which is not identical with the applied field, owing to the Lorentz internal field, which arises because each dipole is influenced by all the other dipoles. Of course, the dipoles near the surface must feel a different local field from those in the bulk, since they mostly have dipoles on one side which are acting upon them. This should have an influence upon the optical properties of the crystal surface. We have calculated the variations of the local field near the surface and also the optical properties.

Actually, only the atoms in the one or two layers near the surface see a local field which is appreciably different from that of the bulk. This fact comes as a surprise to those who think of the local field as a long-range effect. However, this statement is easy to verify. Assume that we have an electromagnetic wave of frequency ω. The vector potential and atomic polarization at an atomic site $\mathbf{R}_j$ are $\mathbf{A}(\mathbf{R}_j)$ and $\mathbf{P}(\mathbf{R}_j)$. Then Maxwell's equations in the Coulomb gauge give

$$\mathbf{P}(\mathbf{R}_j)=\boldsymbol{\alpha}(\omega)\cdot\Big[(i\omega/c)\mathbf{A}(\mathbf{R}_j)-\sum_{j'}{}' \boldsymbol{\phi}(\mathbf{R}_j-\mathbf{R}_{j'})\cdot\mathbf{P}(\mathbf{R}_{j'})\Big], \quad (1.1)$$

$$\nabla^2\mathbf{A}(\mathbf{r})+(\omega^2/c^2)\mathbf{A}(\mathbf{r})=(i4\pi\omega/c)\sum_j \hat{e}\hat{e}\cdot\mathbf{P}(\mathbf{R}_j)\delta(\mathbf{r}-\mathbf{R}_j), \quad (1.2)$$

where $\boldsymbol{\alpha}(\omega)$ is the atomic polarizability, $\hat{e}$ is the direction of polarization, and $\boldsymbol{\phi}$ is the dipole-dipole interaction:

$$\boldsymbol{\phi}(\mathbf{R})=(\mathbf{I}-3\hat{R}\hat{R})R^{-3}. \quad (1.3)$$

We simplify the problem by setting the incident light normal to the surface. We also assume that the surface was created by cleaving, so the atoms are in planes that run parallel to the surface. In order to keep the mathematical discussion as simple as possible, we are just going to discuss the three cubic structures sc, bcc, and fcc. These crystals have sufficient symmetry so that within a plane all atoms are in equivalent positions. Denote the various planes by l, where $l=1, 2, 3, 4, \cdots$ going inward from the surface. Now $\mathbf{P}(\mathbf{R}_j)$ and $\mathbf{A}(\mathbf{R}_j)$ need only be described by their value of l, $P(l)$ and $A(l)$, since all values in the same plane are equal. Hence (1.1) and (1.2) simplify to

$$P(l)=\alpha(\omega)\Big[(i\omega/c)A(l)-(4\pi/V_0)\sum_{l'} v(l-l')P(l')\Big], \quad (1.4)$$

$$(\partial^2/\partial x^2)A(x)+(\omega^2/c^2)A(x)=(i4\pi\omega a/cV_0)\sum_l P(l)\delta(x-la). \quad (1.5)$$

The values of $v(l)$ are obtained by summing the dipole-dipole interaction over all the atoms in the plane:

$$v(l)=(V_0/4\pi)\sum_{\rho j}\hat{z}\cdot\boldsymbol{\phi}(\mathbf{R}_j)\cdot\hat{z}.$$

We have removed the factor $4\pi/V_0$, where V_0 is the volume of a unit cell, so as to make $v(l)$ dimensionless. The distance between planes is a. Table I shows some calculated values of $v(l)$ for the various cubic lattices, where $\mathbf{k}$ is in a $\langle 100\rangle$ direction. These were evaluated by the planewise summation method of Nijboer and de Wette.[1,2] This method is described in Appendix A. The

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[1] B. R. A. Nijboer and F. W. de Wette, Physica 24, 422 (1958); 23, 309 (1957).

[2] F. W. de Wette and G. E. Schacher, Phys. Rev. 137, A78 (1965).

dipole interaction falls off very rapidly as the distance between planes increases. In general, one need only to sum over a few neighboring planes in order to obtain accurately the Lorentz-Lorenz value of $-\frac{1}{3}$. One can see in Table I that these values do obey

$$-\tfrac{1}{3}=v(0)+2\sum_{l=1}^{\infty}v(l).$$

This verifies our assertion that the local field mostly comes from nearby planes of atoms.

One can think of $v(l)$ as simply an interaction term between planes of polarization. Since this interaction declines so rapidly with distance, an accurate result can be obtained by only including the interactions between a few neighboring planes. That is, little error is incurred by setting $v(l)=0$ for all l greater than some number N (such as 3 or 4). This simple yet accurate approximation makes it possible to solve (1.4) and (1.5). We have done this and thereby obtained the reflectivity of the surface, and also the values of $P(l)$ near the surface.

The value of N is the maximum number of neighboring planes whose interaction is retained in the calculation. We show that the number of polariton modes[3] in the solid is $N+1$.

So the inclusion of interactions between distant planes in the crystal causes additional polariton modes to propagate in the crystal. Although these extra modes can be plane-wave-like, for most of the cases we have examined they have complex frequency—i.e., they are evanescent. In the optical problem of interest, they will only exist near the surface. Thus, they have little influence upon the dielectric properties of the bulk material, but they can affect the reflectivity of the solid.

Most of us are familiar with surface modes which are also usually evanescent in character. The additional modes in the present problem are not surface modes in the usual sense. They are really just surface parts of the modes which exist in the bulk of the crystal. The modes of the bulk crystal need these surface parts in order to satisfy the boundary conditions at the surface. Each time one includes interaction between additional planes of polarization—say between second, third, or fourth neighbors—one has imposed an additional boundary condition at the surface. The new mode one gets for each additional interaction allows one to satisfy the additional boundary condition.

This calculation may also be viewed as an investigation of spatial dispersion[4,5] from a microscopic point of view. Spatial dispersion applies to phenomena where the dielectric response function $\epsilon(r,t)$ has an r dependence. Or, after Fourier transforming, the dielectric function is $\epsilon(k,\omega)$. Spatial dispersion is the k dependence, which is distinct from ordinary dispersion caused by the frequency dependence. Since the dipole-dipole interaction acts at a distance, the dielectric response function is nonlocal. In other words, one cannot determine the induced polarizability at the surface of the crystal without determining it everywhere self-consistently.

TABLE I. The dipole-dipole coupling $v(l)$ between a dipole and a plane of dipoles at a distance $X=la$ away. These sums are for transverse waves ($\mathbf{P}\perp\mathbf{k}$), where $\mathbf{P}$ and $\mathbf{k}$ are both along $\langle 100\rangle$ directions in these cubic crystals.

	sc	bcc	fcc
$v(0)$	−0.35943	−0.17972	−0.25416
$v(1)$	0.01303	−0.08309	−0.04021
$v(2)$	2.208(−5)	6.515(−3)	6.368(−4)
$v(3)$	4.094(−8)	−2.463(−4)	−7.189(−6)
$v(4)$	7.642(−11)	1.104(−5)	8.511(−8)
$v(5)$	1.427(−13)	−4.724(−7)	−1.000(−9)

There is experimental evidence that spatial dispersion is important in some kinds of optical experiments.[5] So far, most theoretical analyses have been based upon a continuum model of the dielectric, and certain reasonable guesses have been made concerning boundary conditions. These calculations have been quite successful in explaining the relevent experimental data. One of our results has been to verify the boundary conditions used previously. In the cases which we consider, the exact mathematical boundary condition is to set the internal polarization equal to zero at the crystal surface. This is what was usually assumed in prior calculations.

Deutsche and Mead[6] have previously discussed the solution of the problem we are considering. They did not discuss the Lorentz local field problem in particular, but rather the more general problem of the optical properties in the presence of spatial dispersion. Their approach was to first find the normal modes of the polarization field in the absence of the vector potential—that is, to solve (1.4) for $A(l)=0$. Call these normal modes $\psi_l(k)$. They then used these modes as a basis for solving the Eqs. (1.4) and (1.5). Their paper contains a fundamental error. They assumed that the normal modes $\psi_l(k)$ had to be of the form

$$\psi_l(k)=a(k)\,\sin(kl)+b(k)\,\cos(kl). \qquad (1.6)$$

The modes have this form only when one includes interactions between neighboring planes of polarization ($N=1$). Thus, we can use the Deutsche-Mead solution when we consider this case. But we already have noted that when one also includes interactions between more distant planes of polarization, the modes have additional components which are usually evanescent near the surface. In this case, the normal modes do not have the form assumed by Deutsche and Mead. On the other hand, most of their results do not depend upon the

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[3] J. J. Hopfield, Phys. Rev. **112**, 1555 (1958).

[4] S. I. Pekar, Zh. Eksperim. i Teor. Fiz. **33**, 1022 (1957); **33**, 1056 (1957) [English transls.: Soviet Phys.—JETP **6**, 785 (1958); **6**, 813 (1958)].

[5] J. J. Hopfield and D. G. Thomas, Phys. Rev. **132**, 563 (1963); G. D. Mahan and J. J. Hopfield, *ibid.* **135**, A428 (1964).

[6] C. W. Deutsche and C. A. Mead, Phys. Rev. **138**, A63 (1965).

specific form of the normal modes, but just that these modes are an orthonormal set. In fact, we can use some of their results for our reflectivity calculation.

Our method of calculating the reflectivity is much simpler than theirs. One does not need to find the modes $\psi_l(k)$. Nor does one need to solve (1.4) for the polariton modes. Rather, we show that the boundary conditions and reflectivity are obtained exactly for any value of N by solving some simple equations. Since we assume the interaction between the planes depends only on their separation, and since we neglect effects like a slight widening of the lattice near the surface, then standard methods of difference equations can be used. The problem separates into first finding the dispersion in the bulk and then finding and solving the boundary conditions. These results are presented in Sec. II. In Appendix B, we derive the functions $\psi_l(k)$ for $N=1$ and 2. Although these are not needed for the optical calculation, we wish to demonstrate that the Deutsche-Mead assumption (1.6) was incorrect for $N\geq 2$.

II. POLARITON EQUATIONS AND BOUNDARY CONDITIONS

The basic equations were defined in the Introduction. They are the coupled equations for the atomic polarization $P(l)$ and transverse component of the vector potential $A(l)$. We prefer to use the transverse electric field $E_\perp(l)$ instead of the vector potential,

$$E_\perp(l)=(i\omega/c)A(l),$$

so that our coupled equations may be written as

$$P(l)=\alpha(\omega)\left[E_\perp(l)-(4\pi/V_0)\sum_{l'=-N}^{N} v(l')P(l+l')\right], \quad (2.1;l)$$

$$\left[c^2(\partial^2/\partial x^2)+\omega^2\right]E_\perp(x) =(-4\pi\omega^2 a/V_0)\sum_l P(l)\delta(x-la). \quad (2.2)$$

In writing these equations, we have obviously chosen to work in the Coulomb gauge. In this gauge, the transverse field is retarded in time while the dipolar field is instantaneous in time. Any other gauge could have been chosen and the results would be the same. For example, using the Lorentz gauge with retarded dipole interactions leads to exactly the same equations of motion.[7,8] The Coulomb gauge is particularly appropriate for the present problem because of the rapid convergence of the planewise summation method as illustrated in Table I.

In Eq. (2.1), the sum over l' extends to N neighbors. The value of N is rigorously infinity except for exclusions caused by the semifiniteness of the crystal, but we have noted that the values of $v(l)$ fall off very rapidly as l increases. In practice, we only need to take N to be a small and finite number in order to solve the problem with numerical accuracy.

Once the value of N has been selected, then inside of the crystal there are $N+1$ polariton normal modes, as will be shown very soon. Each mode may be characterized by a refractive index n_j, polarization amplitude P_j, and transverse field component E_j. Thus,

$$E_\perp(l)=\sum_{j=1}^{N+1} E_j e^{in_j\Omega l} \quad (2.3a)$$

and

$$P(l)=\sum_{j=1}^{N+1} P_j e^{in_j\Omega l}, \quad (2.3b)$$

where we have introduced the dimensionless frequency

$$\Omega=\omega a/c. \quad (2.4)$$

We shall later need to use $\bar{\alpha}=\alpha/V_0$, the polarizability per unit volume. Deutsche and Mead[6] showed that solving (2.2) and (2.3) yields

$$E_j=\frac{2\pi}{V_0}\frac{\Omega\sin\Omega}{\cos\Omega-\cos(n_j\Omega)}P_j. \quad (2.5)$$

This result appears somewhat strange until one realizes that usually $\Omega\ll 1$, so the trigometric functions may be expanded, and (2.5) is essentially the familiar result

$$(4\pi/V_0)P_j=(n_j^2-1)E_j.$$

This latter result is what one gets in a continuum approximation where the lattice discreteness is overlooked. In order to maintain rigor, the exact result (2.5) will be employed.

Equation (2.5) expresses E_j in terms of P_j. This may be inserted into (2.3a), and the resulting expression for $E_\perp(l)$ put into (2.1). This gives an equation entirely in terms of the P_j:

$$\sum_j P_j e^{i\Omega n_j l}=4\pi\bar{\alpha}\left(\tfrac{1}{2}\sum_j P_j\frac{\Omega(\sin\Omega)e^{in_j\Omega l}}{\cos\Omega-\cos n_j\Omega} -\sum_{l',j} v(l')P_j e^{in_j\Omega(l+l')}\right). \quad (2.6)$$

This is the polariton equation of motion. There is a different equation for each value of l. Now in the ideal case, where the sum over l' in the local field extends over all other planes of atoms in the crystal, this generates an infinite set of equations for the infinite set of unknowns P_j.

In our practical approach, where the sum is taken over a few (N) neighboring planes, the problem can be solved easily. Far inside the crystal surface, actually for $l>N$, the equations for each value of l are the same. Because of this, it can be shown that Eq. (2.6) is satis-

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[7] G. D. Mahan, J. Chem. Phys. **43**, 1569 (1965).

[8] A. Lucas, Physica **35**, 353 (1967).

fied for each value of j individually:

$$1=4\pi\bar{\alpha}\left(\frac{1}{2}-\frac{\Omega\sin\Omega}{\cos\Omega-\cos(n_j\Omega)}-v(0)-2\sum_{l=1}^{N}v(l)\cos(n_j\Omega l)\right). \tag{2.7}$$

This unusual looking equation is actually quite familiar. If we abbreviate

$$T(k)=v(0)+2\sum_{l}v(l)\cos(kal), \tag{2.8}$$

then for $\Omega\ll 1$, (2.7) is just the usual dielectric equation

$$n_j^2-1=4\pi\bar{\alpha}/[1+4\pi\bar{\alpha}T(k)].$$

Some plots of $T(k)$ as a function of k have been given by Lucas.[8] Equation (2.8) would actually be an efficient way of determining this kind of curve.

Equation (2.7) is essentially an $N+1$ degree equation in the variable $\cos(n_j\Omega)$. Its $N+1$ roots correspond to $2(N+1)$ solutions $\pm n_j$, where $j=1, 2, \cdots, N+1$, of which one-half must be ruled out. In contrast to an argument in Ref. 6, this can be done in a well-defined way if one includes the effect of damping (produced, among others, by phonon-phonon interactions) in Eqs. (2.1) and (2.7) by giving the polarizability an imaginary part:

$$\alpha(\omega)=\alpha_0(\omega)+i\gamma(\omega);\quad \bar{\alpha}(\omega)=\bar{\alpha}_0(\omega)+i\bar{\gamma}(\omega).$$

All roots n_j then will be complex, but, since we assume incident radiation only from $x=-\infty$, only the modes which are exponentially damped as $x\to+\infty$ can be excited, i.e.,

$$\mathrm{Im}n_j>0.$$

This prescription, together with (2.7), specifies the $N+1$ allowed polariton modes $n_j(\omega)$, even in the limit of vanishing damping $\gamma(\omega)\to 0$.

We stated above that, for our idealized surfaces, the problem separates into two parts. The first is to determine the $N+1$ polariton modes $n_j(\omega)$ which are obtained by solving (2.7). The second is the boundary problem, to which we now address ourselves. There are $N+3$ amplitudes in the problem: the incident (I) and reflected (R) electric field amplitudes, and the $N+1$ set P_j. The value of I is given, so there are $N+2$ unknowns. E and H conservation provide two boundary conditions, so N additional boundary conditions are needed for the reflectivity calculations.

These N conditions are provided by the special equations satisfied by the N surface layers. These layers ($l=1, 2, \cdots, N$) feel a different local field than layers in the bulk ($l>N$) because their local-field sum must exclude the absent planes ($l\leq 0$). They have an equation

$$P(l)=\alpha(\omega)\left[E_\perp(l)-(4\pi/V_0)\sum_{l'=1-l}^{N}v(l')P(l+l')\right], \tag{2.9;l}$$

where the sum starts at $1-l$ instead of at $-N$ as in (2.1).

The boundary conditions are derived by introducing fictitious polarizations $P(l)$ at the sites of the absent planes $l\leq 0$. At these fictitious sites, $P(l)$ is defined by (2.3b) with $l\leq 0$. Next we note that the introduction of these fictitious layers now makes (2.1;l) valid even into the surface layers $l=1, 2, \cdots, N$. This is true because the eigenvalue condition (2.7) is satisfied for each value of j. So, in the surface layer, we have two different equations, (2.1;l) and (2.9;l), which are both satisfied. By successively subtracting them for each value of $l=N$, $N-1, \cdots, 1$, we obtain the N boundary conditions.

First subtract (2.9:N) from (2.1:N),

$$0=\alpha(\omega)[0+(4\pi/V_0)v(N)P(0)],$$

with the result

$$P(0)=0. \tag{2.10$'$}$$

The same subtraction for $l=N-1$ gives

$$0=\alpha(\omega)\{0+(4\pi/V_0)[v(N)P(-1)+v(N-1)P(0)]\},$$

which, together with (2.10), gives

$$P(-1)=0. \tag{2.10$''$}$$

Continuing until $l=1$, we get

$$P(m)=0,\quad m=0, -1, -2, \cdots, 1-N \tag{2.10}$$

where by $P(m)=0$ we mean (2.3b)

$$P(m)=0=\sum_{j=1}^{N+1}P_je^{im\Omega n_j}.$$

Our interest is in the optical reflectivity. Consider a wave incident upon the crystal face, and part is reflected and part transmitted. At the point $l=1$, the incident amplitude is $Ie^{i\Omega}$ while the reflected amplitude is $Re^{-i\Omega}$. Deutsche and Mead show by solving (2.2) that

$$I=(2i\sin\Omega)^{-1}\sum_{j=1}^{N+1}E_j(e^{in_j\Omega}-e^{-i\Omega}) \tag{2.11a}$$

and

$$R=-(2i\sin\Omega)^{-1}\sum_{j=1}^{N+1}E_j(e^{in_j\Omega}-e^{i\Omega}). \tag{2.11b}$$

Using (2.5), we get

$$I=(i\Omega 2\pi/V_0)\sum_{j=1}^{N+1}P_j(1-e^{-i\Omega(n_j-1)})^{-1}, \tag{2.11c}$$

$$R=(-i2\pi\Omega/V_0)\sum_{j=1}^{N+1}P_j(1-e^{-i\Omega(n_j+1)})^{-1}. \tag{2.11d}$$

Again these results appear more familiar in the limit that $\Omega\ll 1$:

$$I=\tfrac{1}{2}\sum_{j}E_j(n_j+1)=(2\pi/V_0)\sum_{j}P_j(n_j-1)^{-1}, \tag{2.11e}$$

$$R=-\tfrac{1}{2}\sum_{j}E_j(n_j-1)=(-2\pi/V_0)\sum_{j}P_j(n_j+1)^{-1}. \tag{2.11f}$$

The reflectivity problem has $N+2$ unknowns. The incident intensity I is known, while the unknowns are R and the $N+1$ set P_j. They are solved by using the two equations (2.11c), (2.11d), plus the N equations (2.10) which related the P_j among themselves.

We show in Appendix C that the solution of the $N+1$ equations (2.10) and (2.11c) for arbitrary N in the limit $\Omega \ll 1$ yields

$$(4\pi/V_0)P_j = 2I \prod_{m=1}^{N+1} (n_m - 1) / \prod_{k \neq j} (n_k - n_j), \quad (2.12)$$

and that the reflection factor ρ is given by[9]

$$\rho = R/I = -\prod_{m=1}^{N+1} \frac{n_m - 1}{n_m + 1}. \quad (2.13)$$

Note that ρ is the product of reflection factors for the individual modes; the same, of course, holds for the reflectivity r:

$$r(\omega) = |R/I|^2 = \prod_{m=1}^{N+1} \left| \frac{n_m - 1}{n_m + 1} \right|^2. \quad (2.14)$$

The problem has been completely solved. One picks a value of N, and the $N+1$ refractive indices $n_j(\omega)$ are found by solving (2.7). The refractive indices can be inserted into (2.14) to obtain the reflectivity, and the results (2.12), (2.3), and (2.5) can be combined to find $P(l)$ and $E_1(l)$ anywhere inside of the crystal. The calculation may be made arbitrarily accurate by increasing the value of N.

III. DISCUSSION

A physical problem was proposed in the Introduction. The Lorentz local field changes as one gets near the surface of a crystal. Correspondingly, the polarization of each atom changes as one gets near the surface. These two effects are interrelated, and must be determined self-consistently. We have solved this problem, and shown how these changes affect the reflectivity of the solid.

We have considered the simple case where planes of atoms run parallel to the surface. In the monatomic cubic lattices, each atom in a plane sees the same local field as all others in the same plane. So the properties of an atom are specified by the plane, to which we give the label $l=1, 2, 3, 4, \cdots$, where the counting starts from the surface plane. Furthermore, the equations of motion can then be written as having an effective coupling between planes. This coupling arises from the local field potential. We have shown that the coupling between planes decreases exponentially as the separation between planes increases. One only needs to include the coupling between a few neighboring planes of atoms in order to solve the local field problem quite accurately.

If one retains coupling only between N planes while solving the problem, then there are $N+1$ polariton modes inside of the crystal. Each of these $N+1$ modes are characterized by a refractive index n_j, and these indices are obtained as the roots to an $N+1$ degree equation. When we calculated the reflectivity r, the surprising result was found that

$$r(\omega) = \prod_{j=1}^{N+1} \left| \frac{n_j - 1}{n_j + 1} \right|^2.$$

The net reflectivity is the product of the reflectivity from each separate mode.

Most of the $N+1$ refractive indices are complex. At most, only one or two of them will have significant real parts over a given frequency range. Of course, if n_j is totally imaginary, $n_j = i\alpha$, then it contributes nothing to the reflectivity:

$$\left| \frac{i\alpha - 1}{i\alpha + 1} \right|^2 = 1.$$

So if one calculates the reflectance by successively solving with $N=1$, 2, 3, etc., then the additional indices which one gets will probably be largely imaginary so that the calculated reflectance does not change much as N is increased. Also note that if the value of n_j is complex, then this mode only exists at the surface of the crystal and does not contribute to $P(l)$ or $E_1(l)$ as l becomes large inside the bulk of the crystal.

Some numerical calculations were performed of the reflectivity. A simple model of a single oscillator was used:

$$4\pi\bar{\alpha} = 4\pi\beta / [1 - (\omega/\omega_0)^2],$$

and the reflectivity was calculated near its resonance frequency. Calculations were done for a local theory $N=0$, and also $N=1$. For the latter case, $v(1)$ was taken to be its bcc value of -0.08309. In order that the net resonance frequency in each case was identical, we set $v(0) = -\frac{1}{3}$ for $N=0$, and $v(0)+2v(1) = -\frac{1}{3}$ for $N=1$. The two calculated reflectivities were virtually identical. They differed at most in the third significant figure, and graphs of the two calculated reflectivities could not be distinguished. Since $v(1)$ is largest for the bcc case, we expect this case to show the largest difference from $N=0$. Since no significant numerical difference is found between $N=0$ and $N=1$, we conclude that these local field variations near the surface are not important for optical reflectivity effects. This result is physically reasonable after we have shown that the coupling between planes of atoms falls off so rapidly with distance. At that point, it is reasonable that only a few surface planes of atoms will see a local field appreciably different from the bulk, and the properties of a few surface layers of atoms do not generally affect the bulk reflectivity properties.

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[9] For $N=1$, this gives $\rho = (n_1-1)(n_2-1)/(n_1+1)(n_2+1)$. Hopfield and Thomas also considered this case in Ref. 5. They got the same answer, except they wrote it as $(n^+-1)/(n^++1)$, where $n^+ = (n_1 n_2 + 1)/(n_1 + n_2)$.

Of course polariton effects can still affect the reflectivity from crystals. In the cases for which these effects have been shown to be important,[5] there is a large amount of dispersion in the polarization band. This dispersion arises from the effective mass of exciton states, which is caused by exchange and charge overlap between neighboring atoms. Our model excludes these effects, and only considers dispersion from the dipole field. This type of dispersion is very weak compared to the effective-mass contribution. This explains why our reflectivity calculations showed such little polariton effects. Of course, we could probably include these exchange-type effects by having $v(1)$ be a parameter which included these terms also, but we have not yet tried this extension.

APPENDIX A: PLANEWISE SUMMATION

The method of planewise summation was introduced by Nijboer and de Wette.[1] Formulas for a wide variety of cases have been presented by de Wette and Schacher.[2] The formulas needed for our calculation will be summarized here. They have been obtained by using the method given in these two references.

Basically, one wants to sum the dipole-dipole interactions over all of the atoms in a plane:

$$\mathbf{V}(\mathbf{X})=\sum_{\rho j}\phi(\mathbf{R}_j)\,,$$

where $\mathbf{R}_j=(\mathbf{X},\boldsymbol{\rho}_j)$. The lattice vectors in the plane are $\boldsymbol{\rho}_j$, while $\mathbf{X}$ is normal to the plane. For the case of present interest where radiation is normal to a surface, then $\boldsymbol{\rho}_j$ is in the (Y,Z) plane, and we want the ZZ component of V. Also, $X=la$, where a is the separation between planes and l is the number of planes away. Thus,

$$V(l)=\hat{z}\cdot\mathbf{V}\cdot\hat{z}=\sum_{\rho j}(1-3\rho_z^2/\rho^2)/R^3\,,$$

$$R=[\rho^2+(la)^2]^{1/2}\,.$$

Two separate formulas are necessary to obtain the numbers in Table I. The easiest is when $l\neq 0$. The result obtained from Refs. (1) and (2) is

$$V(l)=(2\pi/A)\sum_{G\neq 0}(G_z^2/G)e^{-G|l|a}\cos(\boldsymbol{\rho}_0\cdot\mathbf{G})\,,$$

where A is the two-dimensional area of the lattice cell in the plane being summed, and $\mathbf{G}$ are the reciprocal-lattice vectors of this plane. The vector $\boldsymbol{\rho}_0$ is obtained by defining $R_0=(X,\boldsymbol{\rho}_0)$ as the vector from where the dipole sum is being evaluated to any atom in the plane. Then $\cos(\mathbf{G}\cdot\mathbf{R}_0)=\cos(\mathbf{G}\cdot\boldsymbol{\rho}_0)$ is independent of the choice of atoms in the plane. The dimensionless $v(l)$ are obtained from $V(l)$ by

$$v(l)=(4\pi/V_0)^{-1}V(l)\,,$$

where V_0 is the volume of the crystal cell.

Another formula is needed for $v(0)$. It is really not necessary to evaluate this case, since the result may be obtained implicitly from the sum rule for cubic crystals:

$$-\tfrac{1}{3}=v(0)+2\sum_{l=1}^{\infty}v(l)\,.$$

Nevertheless, it is usually worthwhile to evaluate $v(0)$ as a numerical check.

There are two different formulas for $V(0)$. One applies if the point at which the dipole sum is being evaluated is not a lattice site. Then let $\boldsymbol{\rho}_0$ be the vector to any lattice point from the position where the dipole sum is desired. Thus,

$$V(0)=\frac{1}{\Gamma(\frac{3}{2})}\left\{\sum_j\frac{(1-3\cos^2\theta)}{(\boldsymbol{\rho}_j-\boldsymbol{\rho}_0)^3}\Gamma\left(\tfrac{3}{2},\frac{\pi}{\eta^2}(\boldsymbol{\rho}_j-\boldsymbol{\rho}_0)^2\right)-\frac{\pi^{3/2}}{\eta A}\right.$$
$$-\frac{\pi}{4A}\sum_G{}'\,G\cos(\mathbf{G}\cdot\boldsymbol{\rho}_0)\Bigg[\Gamma(-\tfrac{1}{2},\beta)(1+\cos(2\theta'))$$
$$\left.-\frac{2\cos(2\theta')}{\beta^{3/2}}(1-e^{-\beta})\Bigg]\right\}\,,$$

where $\beta=G^2\eta^2/4\pi$, θ is the angle between Z and $\boldsymbol{\rho}_j-\boldsymbol{\rho}_0$, while θ' is the angle between $\hat{Z}$ and $\mathbf{G}$.

The second formula for $V(0)$ applies when $\rho_0=0$ and the origin is a lattice point. Here the result is

$$V(0)=\frac{1}{\Gamma(\frac{3}{2})}\left\{\sum_j{}'\frac{(1-3\cos^2\theta)}{\rho_j^3}\Gamma(\tfrac{3}{2},\pi\rho_j^2/\eta^2)\right.$$
$$-\frac{\pi^{3/2}}{\eta A}+\frac{\pi^{3/2}}{3\eta^3}-\frac{\pi}{4A}\sum_G{}'\,G\Bigg[\Gamma(-\tfrac{1}{2},\beta)(1+\cos 2\theta')$$
$$\left.-2\frac{(1-e^{-\beta})}{\beta^{3/2}}\cos 2\theta'\Bigg]\right\}\,.$$

The primes on summation mean the $\mathbf{G}=0$ or $\boldsymbol{\rho}_j=0$ term is omitted. The parameter η is arbitrary and is chosen so that both summations converge rapidly. For computational purpose we note that the incomplete Γ functions are related to complementary error functions:

$$\Gamma(\tfrac{3}{2},x)=(\tfrac{1}{2}\sqrt{\pi})\,\mathrm{erfc}(\sqrt{x})+(\sqrt{x})e^{-x}$$

and

$$\Gamma(-\tfrac{1}{2},x)=-(2\sqrt{\pi})\,\mathrm{erfc}(\sqrt{x})+2e^{-x}/\sqrt{x}\,.$$

APPENDIX B: SOLUTION WITH $E_\perp(l)=0$

We will now solve the polarization equations for $E_\perp(l)=0$. These provide the normal modes $\psi_l(k)$, which were discussed by Deutsche and Mead.[6] The cases $N=1$ and $N=2$ will be treated in detail. Our main intention is to demonstrate that the form (1.6) assumed by Deutsche and Mead is not valid for $N>1$. This result invalidates their conclusion that refractive indices are only meaningful when the interaction between planes of atoms has the form of their equations (58) or (60).

The modes $\psi_l(k)$ have no physical significance whatsoever. Some mistakenly believe that $E_\perp(l)$ is an "applied" field, and in the absence of such an applied field, then $\psi_l(k)$ are normal modes of the polarization field. This is not true. The polarization field is composed of radiating dipoles which generate their own electromagnetic field. The field $E_\perp(l)$ enters the definition of the normal modes (polaritons) whether or not an external source is illuminating the crystal. The proper physical picture[3] is that the polariton modes are the normal modes of the crystal, and shining light on the sample just excites these normal modes. Determining the amplitude of these polariton modes is a boundary problem, and that is the subject of the text of this paper.

The modes of a slab of finite thickness will be discussed. This is a departure from the text, where a semi-infinite crystal was treated. The slab has L planes of atoms ($l=1, 2, \cdots, L$).

N=1. The normal-mode equations are

$$\begin{aligned} \psi_l &= -4\pi\bar{\alpha}[v(0)\psi_l+v(1)(\psi_{l-1}+\psi_{l+1})], \quad l\neq 1, L \\ \psi_1 &= -4\pi\bar{\alpha}[v(0)\psi_1+v(1)\psi_2], \qquad \text{(B1)} \\ \psi_L &= -4\pi\bar{\alpha}[v(0)\psi_L+v(1)\psi_{L-1}]. \end{aligned}$$

The polarizations at each end of the crystal, ψ_1 and ψ_L, obey an equation which is different from any interior polarization. These two special equations are the boundary conditions. One can alternatively view the boundary conditions as the assertion that $\psi_0=\psi_{L+1}=0$.

Let us assume that the general solution has the form of (1.6), which leads to the condition for the eigenvalues λ_k:

$$1=-4\pi\bar{\alpha}(\lambda_k)[v(0)+2v(1)\cos ka].$$

We must now choose k, $a(k)$, and $b(k)$ such that the two boundary conditions are satisfied, and also the modes are normalized. From $\psi_0=0$, we get $b=0$. From $\psi_{L+1}=0$, we get $k=\pi\alpha/(L+1)$, where $\alpha=1, 2, \cdots, L$. The L choices for α provide the L different normal modes. The final solution is

$$\psi_l(k)=[2/(L+1)]^{1/2}\sin kl. \qquad \text{(B2)}$$

Deutsche and Mead[6] also describe a method of deriving the additional boundary conditions needed to evaluate the reflectivity. We applied their prescription to our case and obtained the boundary condition $P(0)=0$, which is what we had already deduced in Sec. II.

N=2. We will now solve (1.4) when there are interactions between neighboring and also next neighboring planes of polarization. Thus, we keep as finite $v(0)$, $v(1)$, and $v(2)$, and set the remaining $v(l)$ equal to zero.

The notation is simplified by defining a constant a and a function of frequency $z(\omega)$ as

$$\begin{aligned} 2a &= v(1)/v(2), \\ z(\omega) &= -[v(0)+1/4\pi\bar{\alpha}(\omega)]/v(2). \end{aligned} \qquad \text{(B3)}$$

Then the equations can be written

$$z\psi_l=2a(\psi_{l+1}+\psi_{l-1})+\psi_{l+2}+\psi_{l-2}, \qquad l\neq 1, 2, L-1, L \qquad \text{(B4)}$$

$$\begin{aligned} z\psi_1 &= 2a\psi_2+\psi_3, \\ z\psi_2 &= 2a(\psi_1+\psi_3)+\psi_4, \\ z\psi_{L-1} &= 2a(\psi_L+\psi_{L-2})+\psi_{L-3}, \\ z\psi_L &= 2a\psi_{L-1}+\psi_{L-2}. \end{aligned} \qquad \text{(B5)}$$

In this case, there are four special equations: two at each end of the solid. Note that a solution of the type (1.6) can no longer work. One can not satisfy these four special equations with the two constants $a(k)$ and $b(k)$, especially since one of them is a normalization constant. However, let us see what happens when $\sin kl$ or $\cos kl$ is tried as a solution to (B4). Both sine and cosine satisfy the equation, and produce an eigenvalue relation

$$z(\omega)=4a\cos k+2\cos 2k. \qquad \text{(B6)}$$

For each allowed value of k, this equation determines the eigenvalue $\lambda_k=\omega$. We specify below how the allowed values of k are found.

Let us turn (B6) around and ask: Given the eigenvalue λ_k, what is the value of k? Note that this is basically a quadratic equation for $\cos k$,

$$\cos^2 k+a\cos k-\tfrac{1}{4}(2+z)=0. \qquad \text{(B7)}$$

So there are two values of k which satisfy this relation for each λ_k. The normal modes at a given frequency are described by two wave vectors rather than just one. Thus, the normal modes are really of the form

$$\psi_l(k)=a(k)\sin(kl)+b(k)\cos kl + c(k)\sin k'l+d(k)\cos k'l, \qquad \text{(B8)}$$

where $\cos k$ and $\cos k'$ are the two solutions to the quadratic equation (B7). Although k and k' both vary with frequency, they are not independent functions. One simple way to express their relationship is

$$-a=\cos k+\cos k'. \qquad \text{(B9)}$$

There is a simple way to find both the eigenvalue equation and also the eigenfunctions $\psi_l(k)$. Equations (B5) are equivalent to the choice of the four boundary conditions,

$$0=\psi_0=\psi_{-1}=\psi_{L+1}=\psi_{L+2}. \qquad \text{(B10)}$$

All that one needs to do is to use (B8) and (B10) to solve for the coefficients a, b, c, and d. These conditions, along with the normalization requirement on $\psi_l(k)$, are sufficient to determine all of the coefficients a, b, c, and d as well as providing the eigenvalue condition.

This completely specifies how to find the normal modes for $N=2$. For $N=3$, we get a cubic equation for $\cos k$ so there are three wave vectors k, k' and k''. Correspondingly, $\psi_l(k)$ now has six terms and six coefficients a, b, c, d, e, and f. One determines them, as well as the eigenvalues, by the boundary conditions that $0=\psi_0$

$=\psi_{-1}=\psi_{-2}=\psi_{L+1}=\psi_{L+2}=\psi_{L+3}$. The extension to higher values of N is obvious.

The assumption (1.6) of Deutsche and Mead[6] is incorrect because they failed to realize that increasing N introduced additional wave vectors into the problem.

APPENDIX C: SOLUTION FOR GENERAL N

We wish to obtain the $N+1$ amplitudes P_j by solving the $N+1$ equations (2.11c) and (2.10) for $m=1, 2, \cdots, N$. The notation is simplified by denoting $X_j=e^{-i\Omega n_j}$ for $j=1, 2, \cdots, N+1$, and $X_0=e^{-i\Omega}$. Then (2.11c) and (2.10) read

$$\sum_{j=1}^{N+1} (X_j-X_0)^{-1}P_j=-\frac{iIV_0}{2\pi\Omega X_0} \tag{C1a}$$

and

$$\sum_{j=1}^{N+1} X_j^{l-1}P_j=0,\quad l=1, 2, 3,\cdots,N. \tag{C1b}$$

Let us write these inhomogeneous equations in matrix form:

$$\mathbf{A}\cdot\mathbf{P}=\mathbf{Q},$$

where A is a $(N+1)$ square matrix with components

$$a_{ij}=(X_j-X_0)^{-1},\quad i=1$$
$$a_{ij}=X_j^{i-2},\quad i=2, 3, \cdots, N+1$$

and $\mathbf{P}=(P_j)$, and $\mathbf{Q}=-iIV_0/(2\pi\Omega X_0)(1,0,\cdots,0)$. The solution in terms of the cofactor A_{ik} is

$$P_j=\frac{\sum_k A_{kj}Q_k}{\det A}=-\frac{iIV_0}{2\pi\Omega X_0}\frac{A_{1j}}{\det A}. \tag{C2}$$

By expanding $\mathbf{A}$ with respect to the first line, we get $\det A$ in terms of the A_{ik}:

$$\det A=\sum_{i=1}^{N+1} (X_i-X_0)^{-1}A_{1i}. \tag{C3}$$

The determinant of a matrix whose components are $a_{ij}=X_j^{i-1}$ has the value

$$\det|X_j^{i-1}|=\prod_{k>l} (X_k-X_l). \tag{C4}$$

The cofactor A_{1i} has this form, except that the ith row is absent:

$$A_{1i}=(-1)^{1+i}\prod_{\substack{k>l=1\\ \neq i}}^{N+1} (X_k-X_l). \tag{C5}$$

Next we multiply (C3) by the factor $\prod_m (X_m-X_0)$ and insert (C5). This term we call D:

$$D=\prod_{m=1}^{N+1} (X_m-X_0)\det A$$
$$=\sum_{i=1}^{N+1} (-1)^{1+i}\prod_{m\neq i} (X_m-X_0)\prod_{\substack{k>l=1\\ \neq i}}^{N+1} (X_k-X_l).$$

Combining products gives

$$D=\sum_{i=1}^{N+1} (-1)^{1+i}\prod_{\substack{k>l=0\\ \neq i}}^{N+1} (X_k-X_l).$$

This result may be written as a determinant by using (C4):

$$D=-\begin{vmatrix} 0 & 1 & 1 & 1 & \cdots & 1 \\ 1 & 1 & 1 & 1 & \cdots & 1 \\ X_0 & X_1 & X_2 & X_3 & \cdots & X_{N+1} \\ X_0^2 & X_1^2 & X_2^2 & X_3^2 & \cdots & \\ X_0^3 & & & & & \\ \vdots & \vdots & \vdots & \vdots & & \vdots \\ X_0^N & X_1^N & & & \cdots & X_{N+1}^N \end{vmatrix}.$$

We subtract the second line from the first, then

$$D=\begin{vmatrix} 1 & 0 & 0 & 0 & \cdots & 0 \\ 1 & 1 & 1 & 1 & \cdots & 1 \\ X_0 & X_1 & X_2 & X_3 & \cdots & X_{N+1} \\ X_0^2 & X_1^2 & X_2^2 & X_3^2 & & \\ \vdots & \vdots & & & \cdots & \vdots \\ X_0^N & X_1^N & & & \cdots & X_{N+1}^N \end{vmatrix}.$$

Again this has the form (C4):

$$D=\prod_{k>l=1}^{N+1} (X_k-X_l).$$

Now we are able to evaluate P_j. In (C2), we multiply numerator and denominator by $\prod_m (X_m-X_0)$ and get

$$P_j=-\frac{iIV_0}{2\pi\Omega X_0}\frac{1}{D}\prod_{m=1}^{N+1} (X_m-X_0)A_{1j},$$
$$P_j=\frac{iIV_0}{2\pi\Omega X_0}\Big[\prod_{m=1}^{N+1} (X_m-X_0)\Big/\prod_{k\neq j} (X_k-X_j)\Big]. \tag{C6}$$

This is the desired result; all polarization amplitudes are expressed by I and the refraction indices. The reflection factor $\rho=R/I$ remains to be calculated. If we start, for this purpose, from Eq. (2.11f) instead of (2.11e), everything goes through as above except $I\rightarrow -R$ and $X_0\rightarrow X_0^*=1/X_0$. So instead of (C6) we get

$$P_j=-\frac{iRV_0X_0}{2\pi\Omega}\Big[\prod_{m=1}^{N+1} (X_m-X_0^*)\Big/\prod_{k\neq j} (X_k-X_j)\Big]. \tag{C7}$$

Dividing (C6) by (C7) gives

$$\rho=-\frac{1}{X_0^2}\prod_{m=1}^{N+1}\left(\frac{X_m-X_0}{X_m-X_0^*}\right).$$

This is the final result. The reflectivity is the product of the individual mode reflectivities. For $\Omega\ll 1$, we can simplify this to

$$\rho=-\prod_{m=1}^{N+1}\left(\frac{n_m-1}{n_m+1}\right).$$